

CIRCULATION COPY  
SUBJECT TO RECALL  
1 YEAR WEEKS

UCRL- 96160  
PREPRINT

# OPTICAL PROPERTIES OF $\text{CR}^{3+}$ IN FLUORIDE HOSTS

S. A. Payne  
L. L. Chase  
W. F. Krupke

This paper was prepared for submittal to  
1987 International Conference on Luminescence  
Beijing, China, August 17-21, 1987

June 1987

Lawrence  
Livermore  
National  
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

#### **DISCLAIMER**

**This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.**

# OPTICAL PROPERTIES OF $\text{Cr}^{3+}$ IN FLUORIDE HOSTS\*

Stephen A. PAYNE, L. L. CHASE, and William F. KRUPKE

Lawrence Livermore National Laboratory, University of California,  
Livermore, California 94550

We will present information which suggests that the lattice relaxation around a  $\text{Cr}^{3+}$  impurity must be accounted for when interpreting the optical spectra of the ion. Special attention is given to fluoride lattices in which the cation radius is larger than that of  $\text{Cr}^{3+}$ .

## 1. INTRODUCTION

The understanding of the properties of transition metal ion impurities in insulating hosts is based upon the concept that the crystal environment modifies the  $3d^n$  energy levels of the free-ion.<sup>1</sup> Thus, one initially needs to have information concerning the properties of the ion in free space, and also about the nature of the host site into which the ion, ( $\text{Cr}^{3+}$ , in this case), is to be incorporated. Here, we note that there are two important aspects of the crystal site: the identity of the nearest-neighbor (n.n.) anions, and the size of the host metal ion that is to be replaced. The dependence of the magnitude of the crystal field splitting,  $Dq$ , on the particular n.n. anion has long been rationalized in terms of the spectrochemical series. The influence of the size of the site, on the other hand, might be understood in terms of the simple electrostatic model of crystal field theory. In this article, we will show, however, that the lattice relaxation around the  $\text{Cr}^{3+}$  ion is a particularly important effect that needs to be considered.

---

\*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract # W-7405-ENG-48, and supported by Division of Materials Research Office of Basic Energy Sciences, U.S. Department of Energy.

## 2. RESULTS AND DISCUSSION

### 2.1 Spectroscopy of $\text{Cr}^{3+}$ in $\text{CdF}_2$ , $\text{CaF}_2$ , $\text{SrF}_2$ and $\text{BaF}_2$

The cation site of fluorite-structure hosts is normally eightfold coordinated, although the rather large difference in ionic radius of the host and  $\text{Cr}^{3+}$  ions (e.g. 1.1Å for  $\text{Ca}^{2+}$  versus 0.6Å for  $\text{Cr}^{3+}$ ) assures that some degree of lattice relaxation will take place. In fact, the optical spectra as well as previously reported EPR results<sup>2</sup> indicate that the  $\text{Cr}^{3+}$  site becomes coordinated by six of the eight fluorines.

The absorption and emission spectra of  $\text{Cr}^{3+}$  in  $\text{CdF}_2$ ,  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  are shown in Fig. 1.<sup>3</sup> In agreement with the predictions of the  $d^3$  Tanabe-Sugano diagram in octahedral symmetry, the energies of the  ${}^4\text{A}_2 \rightarrow {}^2\text{E}$  and  ${}^2\text{T}_1$  transitions do not change with host lattice, while the transition energies to the  ${}^4\text{T}_2$  and  ${}^4\text{T}_1$  states do vary somewhat due to differences of the crystal field strength of the various hosts. We cannot account for the absorption bands if it is assumed that the  $\text{Cr}^{3+}$  ions are in eightfold coordination. In Fig. 2 we illustrate the likely mechanism by which the lattice relaxation in the fluorite-structure hosts would produce sixfold coordination.<sup>3</sup>

### 2.2 Spectra of $\text{Cr}^{3+}$ in other fluoride hosts

As discussed above, the  $\text{Cr}^{3+}$  impurity substantially modifies the fluorine positions of the fluorite-structure hosts. If this effect were of a general nature, we would expect to also observe it in crystals having natural octahedral sites. Referring to Table 1, we see that values of  $Dq$  for  $\text{K}_2\text{NaCrF}_6$  and  $\text{K}_2\text{NaScF}_6:\text{Cr}^{3+}$  are nearly the same, despite the larger Sc site.<sup>4</sup> The  $\text{CrF}_3$  and  $\text{ScF}_3:\text{Cr}^{3+}$  systems show a similar

trend. This must mean sufficient relaxation of the n.n. fluorines occurs at the impurity sites so as to result in a n.n. environment that is similar to that of the pure  $\text{Cr}^{3+}$  compounds.

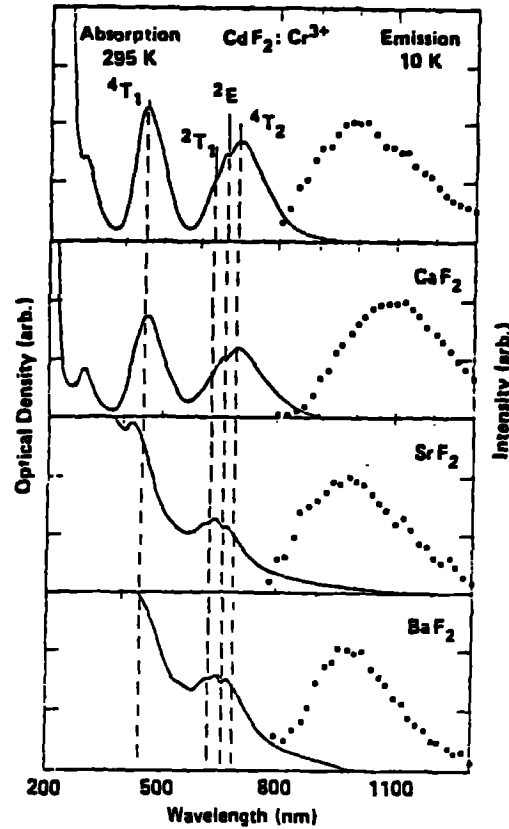


FIGURE 1. Absorption and emission spectra of  $\text{Cr}^{3+}$  in four fluorite-structure hosts. The final states for absorption are indicated for  $\text{CdF}_2$ .

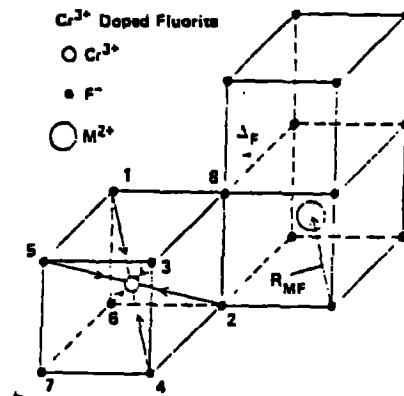


FIGURE 2. Pictorial representation of the relaxation of a ground state  $\text{Cr}^{3+}$  site.

TABLE 1  
Comparison of Sc-containing fluoride crystals  
with pure  $\text{Cr}^{3+}$  compounds at 300K

Crystal	$Dq(\text{cm}^{-1})$	Metal-Anion Distance ( $\text{\AA}$ )
$\text{K}_2\text{NaCrF}_6$	1610	1.93
$\text{K}_2\text{NaScF}_6$	1560	1.99
$\text{CrF}_3$	1460	1.90
$\text{ScF}_3:\text{Cr}^{3+}$	1410	2.01

### 3. CONCLUSIONS

We have found that the net effect of the lattice relaxation is to result in n.n. environments and optical spectra that are more similar than otherwise expected.

### ACKNOWLEDGEMENTS

We wish to thank Mr. Gary Wilke for performing many of the experimental measurements.

### REFERENCES

1. C. J. Ballhausen, Introduction to Ligand Field Theory (McGraw-Hill, New York, 1962).
2. W. Gehlhoff and W. Ulrici, Phys. Stat. Sol. B102, (1980) 11.
3. S. A. Payne, L. L. Chase, and W. F. Krupke, J. Chem. Phys 86 (1987) 3455.
4. G. Huber, S. A. Payne, L. L. Chase, and W. F. Krupke, Submitted to J. Luminesc.